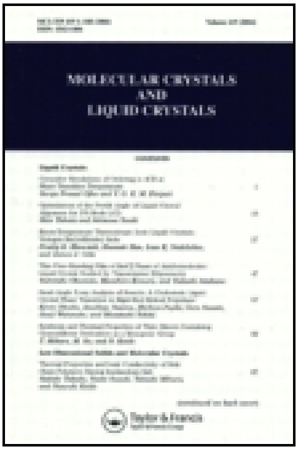

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A p-Phenylene Vinylene Polymer Bridged by a Triazine for Electro-Fluorescence Switching

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A *p*-Phenylene Vinylene Polymer Bridged by a Triazine for Electro-Fluorescence Switching

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A highly fluorescent s-triazine (ST) bridged p-phenylene vinylene (PPV) polymer was synthesized by the Wittig polycondensation reaction of 4, 6-bis (4-formylphenoxy)-2-diphenylamino-s-triazine and 2, 5-bis (triphenylphosphonionmethyl)-1, 4-bis (trimethylsilyl) benzene dibromide, to afford ST bridged PPV polymer (DTTPV). The fluorescence of the polymer was dramatically changed by the application of the external potential from −2 V to 2 V in a two electrode cell containing a solid polymer electrolyte layer. The fluorescence switching was reversible with a switching time of 4s.

Keywords: electro-fluorescence switching; *p*-phenylene vinylene; s-triazine

1. INTRODUCTION

Redox switchable fluorescent materials have been interested for organic electronic and sensing devices [1–9]. The redox-fluorescence switching has been driven from redox active center thus some examples include electrochemically modified conjugated fluorescent polymer or a mixture of a fluorophore with redox couples, which are operating through redox reaction of the polymer or redox quencher in solution. In our previous report, we showed a redox switchable fluorescence cell in which a highly fluorescent and electrochemically

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stable tetrazine doped polymer gel was in contact to a solid polymer electrolyte layer [7]. The fluorescence from the cell was almost extinguished when the cell was applied to a negative potential at which tetrazine was reduced to form anion radical. The cell showed reversible fluorescence modulation with a working voltage less than 3 V. As the solid polymer electrolyte (SPE) interfaced between the counter electrode and fluorescent layer, the two electrode fluorescent device offers a solid-phase device convenient for practical device fabrication. Such device could be extended to fluorescent polymers such as *p*-phenylene vinylene (PPV) polymers.

Herein, we report the synthesis and reversible fluorescence switching of 1,3,5-Triazine (ST) ST copolymer, bridged with PPV unit.

2. EXPERIMENTAL

2.1. General Information

The molecular weight average of the polymer was characterized by gel permeation chromatography (GPC) (model: Waters R-401 ALC/GPC) with THF as an eluent and polystyrene standard for calibration. Fluorescence of the device was measured with luminescence spectrometer (PerkinElmer, Model LS55). FT-IR was taken from a Bruker Vector 22 FT-IR spectrometer. ^{1}H-NMR was recorded on a Varian Inova 400 MHz spectrometer in a $CDCl_3$ solvent and tetramethyl silane as standard. The optical spectra were recorded using a UV-2550 (Schimadzu Co.) spectrophotometer. The electrochemical measurements were made with a universal potentiostat [model CHI 62 4B (CH Instruments, Inc.)] fitted with a two-electrode cell. The illumination of the films of the polymer was performed with a UV lamp (Spectroline, U.S.) model ENF-260/FE (230 V, 50 Hz, 0.17 Amps).

2.2. Materials

Cyanuric chloride, 4-hydroxybenzaldehyde (HBD) and diphenyl amine, potassiumtert-butoxide, triphenylphosphine were obtained from Aldrich and used without purification. 2-Diphenylamino-4, 6-dichloro-s-triazine (1) was prepared according to the reported procedure [10]. Methoxy poly(ethylene glycol) monomethacrylate (MPEGM) (M_n 1000) was purchased from Polyscience, Inc. Poly(ethylene glycol) dimethacrylate (PEGDMe) (M_n 550) and Triallyl-1,3,5-triazine-(1H,3H,5H)-trione (TATT) were obtained from Aldrich. Lithium trifluoromethanesulfonate (LiTFS) was purchased from Merck. Solvents such as acetone, dimethylformamide (DMF), chloroform tetrahydrofuran (THF), and methanol were purified using reported procedures.

2.3. Synthesis of DTTPV

Wittig poly-condensation reaction was used for the polymerization [11]. To a stirred chloroform (25 ml) solution of 4, 6-bis (4-formylphenoxy)-2-diphenylamino-s-triazine (2, 1.0 g , 2.0 mmol) and 2, 5-bis (triphenylphosphonionmethyl)-1, 4-bis (trimethylsilyl) benzene dibromide (3, 2.19 g, 2.0 mmol) was added the methanol (10 ml) solution of potassium tert-butoxide 0.67 g (6.0 mmol) dropwise in 10 minutes. Colour changes to yellow after addition of the catalyst. The reaction was continued for 24 h at ambient temperature. Undissolved solid products were filtered off and the solvent in the filtrate was removed on rotary evaporator to afford polymers. The polymer was purified by reprecipitation using chloroform and *n*-hexane, to give yellow colored solids which was dried in vacuum at 50°C for 12 h. Hydrochloric acid (2%) was added and the by-products, triphenylphosphine oxide and KBr, were removed by filtration. After solvent evaporation on a rotary evaporator, the resultant polymeric product was refluxed for 5 h in toluene in the presence of catalytic amount of iodine, to afford trans product after isolation and purification by reprecipitation from MeOH as yellow colored solids (48% of isolation yield): FT-IR (cm^{-1}, neat film): 1605 (–C=O, end group), 1512 (C=N), 1108 (–C–O–C–) and 960 (trans vinylene). ^1H NMR (400 MH_z, $CDCl_3$, δ ppm): 7.77–6.84 (m, aromatic + vinylene protons), 0.56 (s, 18 H, $-Si(CH_3)_3$).

2.4. Preparation of Electrofluorescent Cell

A polymer electrolyte composition was prepared by mixing MPEGM (0.3 g), PEGDMe (0.6 g), TATT (0.072 g), Darocure 1173 (0.06 g), Irgacure 784 (0.003 g), and LiTFS (0.06 g) according to the method reported in literature [12]. One ITO plate was then spin-coated (1700 rpm/min) with the above mentioned polymer solution, after which the layer was cured for 10 min under a 210 nm UV light. A fluorescent solution was prepared by mixing the 4 with MPEGM (0.3 g), PEGDMe (0.6 g), TATT (0.072 g), iodine, tetrabutylammonium iodide(TBAI), and LiTFS (0.06 g) in chloroform solution. The content of 4 in the solution was 5 wt%. The solution was then used to coat a second ITO plate. A solid-type sandwitched device was prepared by inserting the oligomer-polymer electrolyte mixture solution between a bare ITO electrode and a solid polymer electrolyte-coated ITO electrode. The device was sealed with epoxy resin.

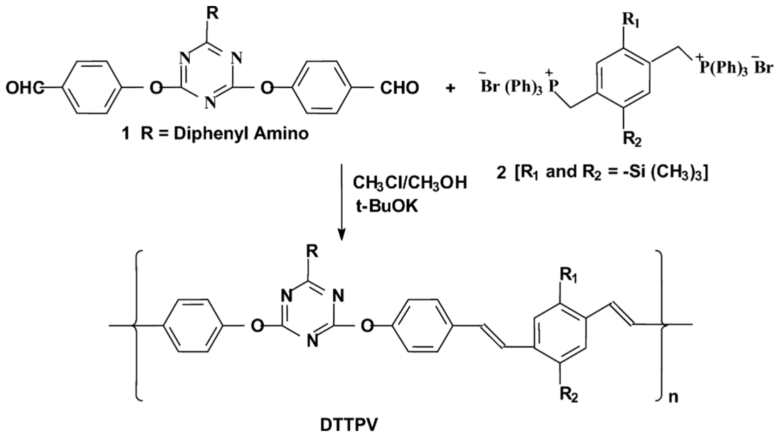
3. RESULT AND DISCUSSIONS

Wittig poly-condensation reaction [11] of 4, 6-bis(4-formylphenoxy)-2-(diphenylamino)-s-triazine (1) with 2, 5-bis (triphenylphosphonion-methyl)-1, 4-bis(trimethylsilyl) benzene dibromide (2) gave the fluorescent s-triazine (ST) bridged *p*-phenylene vinylene (PPV) polymer (DTTPV) as summarized in Scheme 1. Due to the ST unit, the π-electron conjugation of PPV to next PPV units is prohibited by the s-triazine.

The structure of the polymer was confirmed by FT-IR and proton NMR analysis. Strong peaks at 1547 and 976 cm^{-1} due to >C=N- of the triazine nucleus and vinylene structure of the PPV unit of the polymer, respectively, were observed from FT-IR spectra (Fig. 1).

The resulting polymer was soluble in common organic solvents such as chloroform, THF, acetone, ethyl acetate, etc. The chloroform solution of the polymers showed strong fluorescence at 431 nm when excited at 340 nm. The quantum yield for the emission in the solution was determined as 0.41 (referenced to quinine sulfate), which is comparable with the PPVs reported in the literature with fluorene and alkyl spacers [13]. Figure 2 shows the absorption and emission spectra of the polymers in chloroform solution (10^{-6} g/mol).

The cell was prepared as follows. First, an ITO plate was carefully coated with a photo curable polymer electrolyte solution [13] using spin coating method, and then cured with UV light so that it became a stiff film. Then the other ITO plate was coated with a layer of the polymer electrolyte solution containing DTTPV, iodine and TBAI.



SCHEME 1 Synthesis of DTTPV.

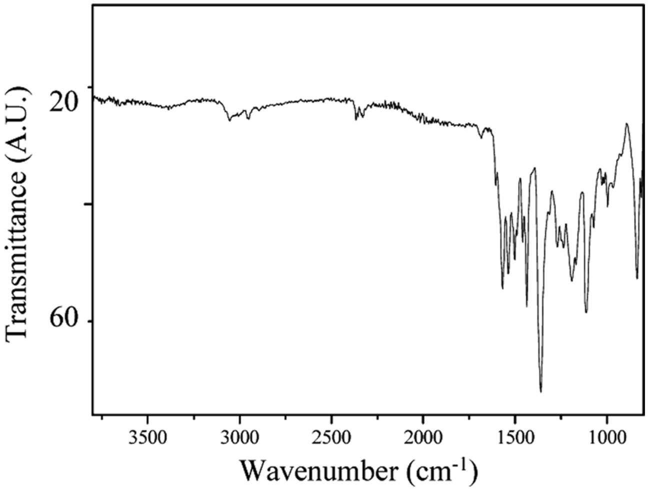


FIGURE 1 FT-IR spectrum of DTTPV.

The two plates were then made to contact, taking care to avoid bubble formation at the interface, and firmly held together before they were connected to a standard potentiostat. The two ITO electrodes were used as working and counter electrodes, respectively, to complete

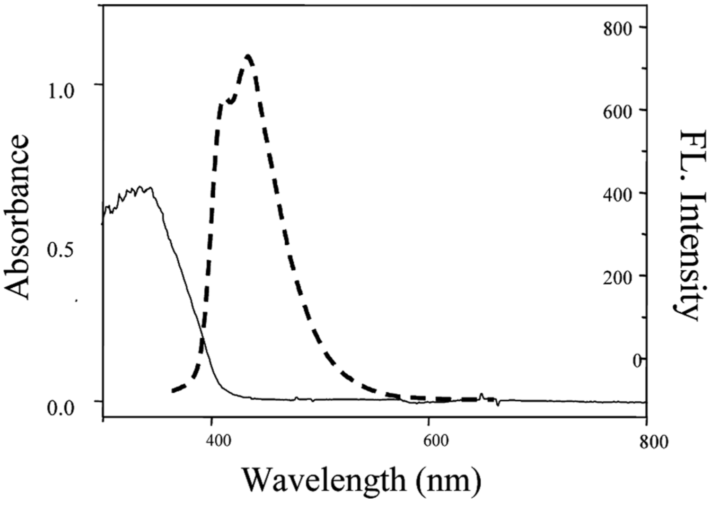


FIGURE 2 UV-Vis (solid) and fluorescence (dashed) spectrum of DTTPV in chloroform.

the two-electrode system. Figure 3 shows CV curve obtained from the two electrode cell, indicating the redox process $>1.2\,\text{V}$, which is the lower limiting potential for the redox-fluorescence switching.

Figure 4 shows the fluorescence spectra of the cell recorded under a light excitation (λ_{exc}) of 400 nm. The fluorescence intensity was dependent upon the applied potential and almost reversibly extinct upon potential scanning toward negative values. Such an electro-fluorescence switching was reversible upon repetitive cycling between $+2\,\text{V}$ and $-2\,\text{V}$ (Fig. 5).

Figure 6 displays a series of pictures showing the fluorescence of the device as a function of the applied electrochemical potentials under UV light illumination ($\lambda_{\text{exc}} = 365\,\text{nm}$). It showed blue emission because of the short conjugation in PPV units which are separated alternatively by ST. Importantly, the device, which is fluorescent at the start, became dark with low emission when a positive potential was applied. The emission was almost extinguished when the applied potential was 2 V (Fig. 6 (a)). However, it became highly fluorescent at $-2\,\text{V}$ (Fig. 6 (b)).

The fluorescent switching in the study could be ascribed to the reversible quenching of the excited state polymer by the redox couple in a two electrode system. Although the detailed mechanism should be further investigated, this study indicates that direct fluorescence switching can be monitored by the electrochemical potential in a solid

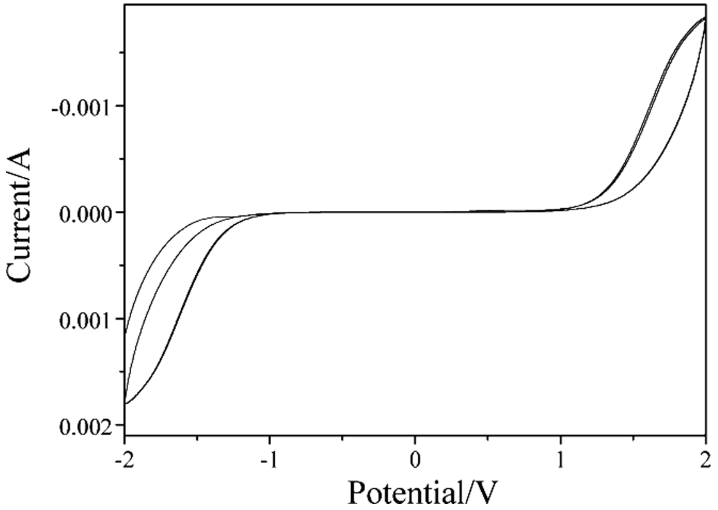


FIGURE 3 CV curve obtained from the cell.

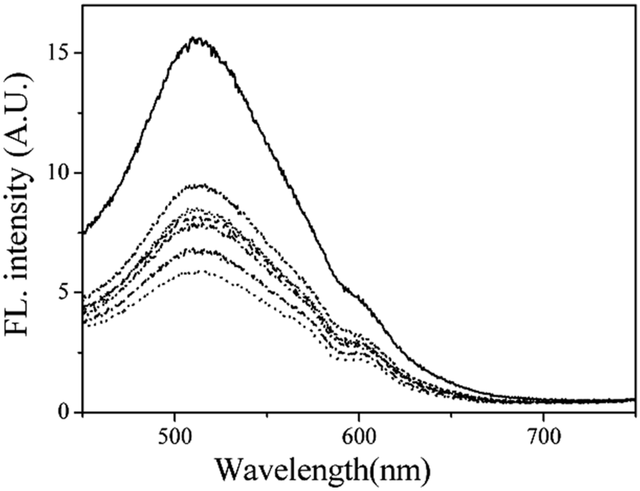


FIGURE 4 Fluorescence spectra of the two electrode cell containing DTTPV at different applied potentials: From top to bottom, −2.0 V, −1.5 V, −1.25 V, 0, 1.25 V, 1.5 V, and 2.0 V.

state cell, in which the new fluorescent ST bridged PPV polymer composite is in contact with a solid polymer electrolyte layer. The redox reaction in this cell requires a very low voltage for the switching.

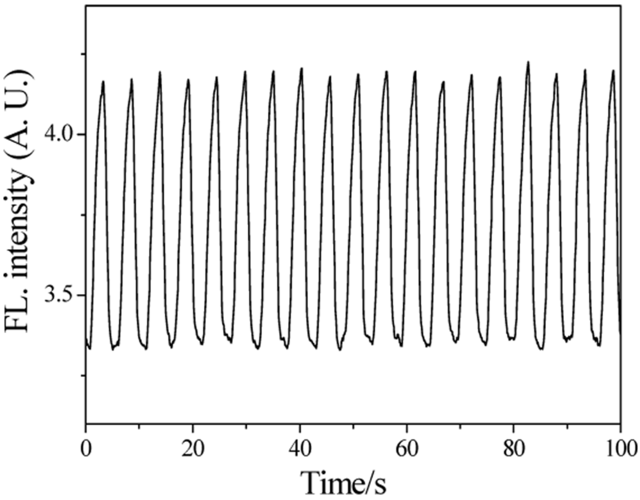


FIGURE 5 Fluorescence modulation of the cell by the potential switching from +2 V to −2 V, 4 sec for each step ($\lambda_{\mathrm{exc}} = 400\,\mathrm{nm}$).

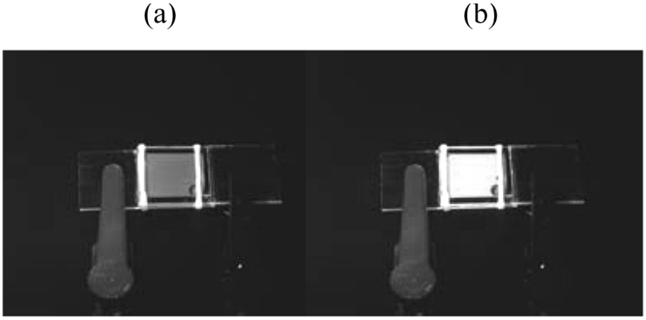


FIGURE 6 Photographic images of the cell emission recorded at different potentials: (a) at $+2\,V$ and (b) at $-2V$ ($\lambda_{exc} = 365\,nm$).

Such a low-voltage working device is important for organic electronics with energy-saving concept. In particular, it could be applied in large display panels operated with a backlight with emittive panels, fluorescent memory, and sensor for imaging reversible redox cycles in living cells [2–9,14].

In conclusion, we synthesized a new fluorescent polymer based on a s-triazine and PPV and demonstrated the feasibility of the redox switching of the fluorescence under a switching voltage of 2 V. The fluorescence switching was reversible with a switching time of 4 s. Further work is in progress to optimize the switching properties of the cell by modifying the fluorescent oligomer structures and electrolyte composition.

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